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The Influence of Manganese on the Growth of Pineapples.

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For a number of years the pineapple growers in the Wahiawa district have observed that on certain sections of their land pineapples do not grow well. On these areas the young plants begin to grow as on the best soils, but in the course of a few months the leaves begin to show a reddish-purple color, which soon gives place to a yellowish-white appearance, and this color persists throughout the remaining life of the plant. Many of these plants never bear fruit; that which is produced, however, is always of inferior size and quality. These areas are quite definite and with the rapid expansion of the pineapple fields in recent years, the land thus affecting this crop has been found to be much greater in extent than was formerly thought. All efforts of the best growers, including the application of fertilizers and lime, good tillage, drainage, etc., have failed effectually to change the growth of the pines on these lands.

A number of investigators have from time to time studied the effects of manganese on plant growth. Such studies, however, have involved merely the application of small amounts of manganese to soils. The smallest amount of manganese found in our best pineapple soils is five times greater than the heaviest artificial application made in previous experiments, while in our black soils the amount is 120 times greater. Previous experiments with manganese have been concerned with the possible stimulating effect of minute quantities. In our pineapple districts, manganese is an important element in the soil. The present bulletin is a preliminary report on the first investigation ever made of soils in which manganese is a dominant and determining factor of plant growth.—E. V. Wilcox.

In consideration of the extent of such soil, and its unusual character, the Hawaii Experiment Station has undertaken an extended investigation of the question. This work is still in progress, but it is thought that results of sufficient importance and scientific interest have been obtained to warrant their publication at this time. This bulletin should, therefore, be regarded as a preliminary report, rather than a complete discussion of the subject.

The pineapple growers have noticed for several years that the soil which produces yellow pines in most instances is dark in color, whereas that producing thrifty, green plants is usually red. From this difference in color, it is common in Hawaii to speak of pineapple soils as being red or black, meaning thereby good or poor pineapple soil; and it is in this sense that the terms red and black soils are used in this paper. In addition to this difference in color, the black soils appear to have a finer texture than the red soils. When reasonably dry and in good tilth, the red soil usually has a granular or "shotty" texture, while the black soil, under similar conditions, is reduced to a finer state of division. Upon thoroughly wetting, however, either of these types[1], may be crushed between the fingers to an almost impalpable mass; and indeed, to such a fine state of division that practically all of it will pass through a one hundred mesh sieve. There is, therefore, very little true grit in this section. It should be remembered in this connection that practically all soils of Hawaii are of volcanic origin, and it seems that in this district, a very complete disintegration of the lava has taken place, which, in some places, extends to a depth of thirty feet or more.

In certain other pineapple sections of Oahu, particularly near Pearl City and Pupukea, a similar condition exists, but since there is a larger area devoted to this crop, and a greater extent of black soil in the Wahiawa district than in other sections of the Islands, it was decided to undertake this investigation at Wahiawa. Accordingly, in September, 1908, two extensive series of fertilizer plot experiments were begun; one on red soil, and one on black. There was a twofold object in these experi-

1. The word "type" is not used in this bulletin in its usual sense, but rather for the sake of brevity.

ments,—first, to determine the fertilizer requirements of pineapples in Hawaii; second, to ascertain the cause of pineapple yellowing on the black soil. This bulletin deals with the latter of these only.

At the beginning of these experiments, a number of samples of soil and sub-soil were taken from various parts of the district. About one-half of these were from the black soil, where the pines were very yellow; and one-half from red soil, producing good pines. The samples of soil were taken to a depth of eight inches; and the sub-soil from eight inches to twenty inches below the surface. Each of these samples represents a composite, taken from not less than six different places; and, therefore, the average of the six samples of each type may be looked upon as representing not less than thirty-six different places in the red and black soils, respectively. In the following table is given the average water-free composition of the two types as determined by the methods of The Association of Official Agricultural Chemists.

TABLE I.

Average Composition of	Red Soils	Red Sub-Soil	Black Soils	Black Sub-Soil
Insoluble matter	42.82%	41.42%	35.26%	37.73
Potash (K_2O)	.59	.63	.91	.87
Soda (Na_2O)	.27	.25	.31	.41
Lime (CaO)	.36	.48	.97	.58
Magnesia (MgO)	.39	.38	.47	.41
Manganese oxide (Mn_3O_4)	.37	.20	5.61	4.90
Ferric oxide (Fe_2O_3)	27.82	30.10	22.58	22.96
Alumina (Al_2O_3)	10.04	10.37	15.39	17.20
Phosphorus pentoxide (P_2O_5)	.08	.12	.27	.16
Sulphur trioxide (SO_3)	.11	.08	.17	.06
Volatile matter	15.14	13.74	17.61	13.67
Titanium oxide (TiO_2)	2.01	2.49	.88	1.08
Total	100.03	100.26	100.43	100.03
Nitrogen (N)	.32	.24	.37	.20
Acidity [1]	1235	.....	98	.....

1. Calculated to pounds of CaO per acre foot.

The growers at Wahiawa often refer to their black soils as being sour, and many of them are inclined to attribute the yellow, dwarfed appearance of the crop on this land to this cause. Investigations, in other countries have pointed out that the pineapple plant is very sensitive to acidity[1]. But in view of the fact that the determination of acidity in these soils shows the presence of much less actual acidity in the black soil than in the red soils, (see table above), it seems that, considering this factor only, the black soils should be the more productive of the two. In fact, every sample of the black soil analyzed contained less acidity than any of the red soils, and furthermore, some of the black soils tested were found to be neutral. It, therefore, seems reasonable that some cause other than acidity is bringing about the unfavorable growth. By reference to the previous table, the black soils are shown to contain even more of the so-called plant foods than the red soil, and in this connection, it is especially noteworthy to point out that the black soil is well supplied with nitrogen, phosphoric acid and potash.

It is well known, however, that the usual chemical analysis of a soil is not sufficient to determine its crop producing power; that the chemist often fails to recognize certain conditions in the soil, which have great influence on crops; and further, that the usual chemical anlysis fails to indicate the availability of the elements in the soil; but without discussing this subject further, it is sufficient at this time to say that the application of liberal amounts of various high grade fertilirers, in conjunction with good tillage, drainage, etc., has not resulted in overcoming the yellowing of pines on this land.

The plots of black soil, to which the Station applied nitrogen, phosphorus, potassium and calcium in various forms and amounts do not indicate an effectual remedy for the yellow-stunted growth of pines there. Some of the same applications to red soil, on the other hand, are proving highly satisfactory. What then is the cause of this phenomenon?

By again referring to the previous table, one striking difference in the composition of the two types is apparent, namely, in their manganese content. In order to bring out this point more forcibly, the following table is submitted, which shows the

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1. Bul. 68, Florida Experiment Station, page 697.

complete analysis of the soils containing the maximum, minimum and average percentages of manganese oxide found in each type.

TABLE II.

	BLACK SOILS			RED SOILS		
	Max.	Aver.	Min.	Max.	Aver.	Min.
Insoluble matter	33.45%	35.26%	34.86%	39.07%	42.85%	44.00
Potash (K_2O)	.83	.91	1.06	.76	.59	.59
Soda (Na_2O)	.40	.31	.29	.33	.27	.29
Lime (CaO)	1.39	.97	.36	.29	.36	.24
Magnesia (MgO)	.54	.47	.40	.35	.39	.41
Manganese oxide (Mn_3O_4)	9.74	5.61	3.91	.91	.37	.15
Ferric oxide (Fe_2O_3)	19.65	22.58	26.39	24.98	27 82	27.94
Alumina (Al_2O_3)	15.50	15.39	14.85	14.73	10.04	11.91
Phosphorus pentoxide (P_2O_5)	.21	.27	.18	.10	.08	.03
Sulphur trioxide (SO_3)	.16	.17	.13	.17	.11	.11
Volatile matter	17.73	17.61	16.33	17.84	15 14	13.94
Titanium oxide (TiO_2)	.73	.88	1.54	.23	2.01	.28
Total	100.33	100.43	100.30	99.76	100.03	99.89
Nitrogen (N)	.39	.37	.30	.34	.32	.29

Since the above analyses were made, numerous other samples have been drawn both from red and black soil; and in every instance, the samples drawn from sections where the pines are yellow, have been found to contain large amounts of manganese, whereas, those taken from the red soil, on which thrifty pines grow, contain little of this element. In general, the black soils contain from ten to fifty times as much maganese as the red soils[1].

All the samples previously referred to were drawn from extremes, that is, either from sections which produce very yellow plants, or from soils producing very thrifty, green pines. The yellow and green areas are not separated by sharp lines of division, however, but rather gradually merge the one into the other.

1. It has been previously pointed out that some Hawaiian soils contain large amounts of manganese (see Press Bulletin No. 18, this Station); but no effort has been made to correlate yellowing of pineapples with the occurrence of manganese in the soil.

There is, therefore, an intermediate area surrounding the yellow spots on which the pines show the yellowing effect to a lesser degree. With the view of determining whether the maganese likewise decreases in passing from the black soil to the red, several series of samples from different places, were drawn at regular distances apart, in passing from the black to the red soil. From the analysis of these samples, a very close correlation between the yellow color of the pineapples and the manganese content of the soil was found to exist.

The following table will show the percentages of the oxide of maganese in black, intermediate and red soils.

TABLE III.

	Black.	Intermediate.	Red.
Manganese oxide (Mn_3O_4)	5.61	1.36	.37

It seems, therefore, that some correlation exists between the yellowing of pineapples and the amount of manganese in the soil.

According to Leclerc[1], manganese is an almost universal constituent of soils, and it is often not determined in soil analysis for the reason that it is not usually regarded as a necessary element of plant food, and is thought to have little or no economic importance in crop production. Among all the analyses, to which the author has had access, none have been reported that contain more than a few tenths of one per cent of Mn_3O_4.

The solubility of a substance in the soil, however, determines in a large measure its influence on plant growth. Sodium, for instance, while not usually considered as an essential to plant growth, when present in the form of a soluble salt, is known to exert a marked influence on crops. Wheeler and Hartwell[2], at the Rhode Island Experiment Station, have shown that soluble sodium compounds may even partially take the place of potassium in the development of certain plants and in certain instances sodium may perform a physiological function in the development of these plants. The occurrence of large amounts of soluble sodium compounds in the soil, however, is known to be very detrimental to the growth of the plant. As is well

1. Cited by Schreiber in Revue Generale Agronomique, January, 1906.
2. Nineteenth Ann. Rept. Of R. I. Experiment Station.

known, sodium and potassium are closely related elements and have many properties in common. Maganese and iron are likewise closely related. It has been shown that when certain plants are grown in culture solutions containing very small amounts of iron, the application of a small amount of soluble manganese brings about new vigor and increased chlorophyl production and in this connection the solubility of the maganese and iron in the black soil becomes a matter of interest. The chief function of iron in plants seems to be connected with the production of chlorophyl, and since the general appearance of the yellow pines indicates that the cholorphyl has been affected the possibility of some influence on the part of the manganese at once suggests itself. In this connection, Loew and Sawa in commenting on the work of Birner and Lucanus say: "In regard to the behavior of plants toward manganese compounds but few experiments have been made and these show that manganese cannot replace the related iron in regard to the production of chlorophyl; and that the manganous and manganic phosphate suspended in culture solution can exert an injurious effect." [1]

With the view of determining the solubility of the manganese and iron, a number of samples of both red and black soils were extracted with a one-per cent solution of citric acid. In this determination, 200 grams of air-dried soil, were treated with 2000 cc of one per cent citric acid for forty-eight hours, with occasional shaking. At the end of this time the solution was filtered, and the iron and manganese determined in the filtrate. The following table will show the results, expressed in percentages of air-dried soil : [2]

TABLE IV.

	Black Soil.	Red Soil.
Mn_3O_4	.733%	.028%
Fe_2O_3	.243	.379

Estimating that an acre foot of this soil weighs about 3,500,000 pounds, we find that the black soil contains, on an average, about 23,755 pounds of citrate soluble mangano-manganic oxide

1. Bul. of the College of Agric. Tokio Imp. Univ., Vol. 5, No. 2, p. 162.
2. Average of the determination in six samples.

per acre foot, while the red soil is found to contain only 980 pounds in the same area. It would, therefore, be extremely surprising if this large amount of soluble manganese were without influence in the soil. It is sufficient here to point out the relations between the citrate soluble iron and manganese in the soil. From the table it is shown that these stand in inverse proportions.

In the strong acid digestion of the black soils, it was noticed that considerable frothing or effervescence developed upon slightly heating the same, and subsequently, this was found to be due to the escape of chlorine gas. Numerous samples have been treated with hydrochloric acid, and in every instance, the black soils have been found to liberate large quantities of chlorine; the red soils do not possess this power.

In the determination of volatile combustible matter, it was also observed that after heating the black soil just below redness for some hours the sample still retained some of its dark color; but upon subsequent stronger heating, further loss in weight occurred and the soil took on a dark brown color. From these facts, it seems likely that at least a part of the manganese in the black soil exists in the form of higher oxides. The black color and the liberation of chlorine gas suggest the presence of manganese dioxide, or of sesquioxide of manganese.[1] It is, of course, likely that the dark color is caused in part, at least by organic matter.

It is reported that in some of these fields the first crop of pines, on virgin soil, showed but little yellow color during the first twelve months of their growth. Later, however, these plants became very yellow and almost ceased to grow. With the continued growth of pines on this soil, its color also seems to become darker. A number of the yellow plants were pulled up and it was found that the soil adhering to the larger roots was darker in color than the general soil. Aso reports that wheat grown in solutions containing a small amount of manganous sulphate was found to contain manganese dioxide adhering to the roots.[2] These facts, together with the observation that the cultivation of pines on this soil renders it less adapted

1. See "Soils" by Hilgard, p. 283.

2. Bulletin of the College of Agriculture, Tokio Imperial University, Vol. V, No. 2, page 183.

to the crop, indicates that there is some change brought about in the soil by the crop itself; and since the soil of this entire section has arisen from the disintegration of lava, which, in its original state could not have contained either of the black oxides of manganese, it seems reasonable that in the growth of pines a change in the state of oxidation of the manganese takes place.

In connection with the investigation of the soil, a study of the yellow plants has also been undertaken. It was formerly believed that the etiolated appearance of the pines was caused by some pathological or entomological infestation; but as yet all efforts to determine such infestation have proven fruitless. No insect or fungus, which is known to produce this phenomenon, has been found on these plants The root system of the yellow plants was found to be dwarfed and much less extensive than that of vigorous, green plants. In many instances, the roots are covered with a black coat, and have but little indication of life. The yellow plants possess but few root hairs. The healthy green pines on the contrary have a very extensive root system, sometimes reaching out to a distance of several feet from the plant.

Some analyses of the ash from both the green and yellow plants have been made, and while a sufficiently large number of plants have not been analyzed to warrant positive conclusions, it seems that the entire metabolism of the yellow plants has been disturbed. A number of young plants, about four months old, taken from both red and black soils, and also an equal number of plants two years old, were examined. A composite sample, made up of an equal number of leaves from the same portion of these plants, was analyzed. In the following table the percentages of manganese oxide in the ash of these plants is given:

TABLE V.

	Yellow Pines. (4 months old)	Yellow Pines. (2 years old)	Green Pines (4 months old)	Green Pines. (2 years old)
Mn_3O_4.....	2.12%	1.15%	1.65%	1.68%

In consideration of the very large percentage of easily soluble manganese in this soil it is rather surprising that a higher percentage of this element is not found in the pineapples grown thereon, especially, since it is generally considered, that, in the

presence of soluble substances, plants have the power of taking up these substances in considerable amounts. It is interesting here to note the smaller percentage of manganese in the ash of the yellow plants two years old, than is found in the younger pines. In the case of green plants, the ash is found to contain about the same percentage of manganese in each of the two stages. In this connection, other investigators have found that many other plants contain notable amounts of manganese. Schroder, for instance, found in the ash of the leaves of the Norway spruce 35.53% Mn_3O_4. [1]

The fact that the ash of other plants, such as wheat, barley, etc., grown under normal conditions, contains not only a higher percentage of nitrogen and potash, but also more of these substances in actual pounds, during the advanced growing period, than at maturity, has been pointed out by several investigators. In a very exhaustive investigation of this subject, Wilfarth and Romer[2] at the Ducal Experiment Station, have shown that the decrease of the actual total nitrogen and potash in wheat and barley, as they pass from the growing stage into maturity, can be explained in no other way than that these substances are actually returned to the soil. These inevstigators found that of the potash in wheat and barley at the time of flowering only 58.87% of that in the former, and 64.97% in the latter remained at maturity; and while it is true that potash is necessary to plant growth, and manganese is not usually so considered, the suggested analogy in the two cases is none the less interesting.

Manganese, when applied in small quantities, has been shown by several workers to produce the effect of stimulation. Nagaoka[3] at the Tokio Imperial University, effected an increase in the yield of rice to the extent of 37% by the application of 77 kilos of manganous sulphate per hectar. At the Woburn Experiment station, the stimulating power of manganese on wheat and

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1. Cited from the Bul., College of Agric., Tokio Imp. Uni., Vol. V, No. 2, p. 161.

2. Researches of the Ducal Agric. Expt. Station, on The Assimilation of the Elements of Nutrition by Plants During Different Periods of Their Growth. Die landwirtschschaftlichen, Versuchsstationen, Vol. 63, 1905.

3. Bul., College of Agric., Tokio Imp. University, Vol. VII, No. 1.

other crops has also been determined; and other investigators have found that small amounts of various manganese compounds produce the same effect. The fact, however, that small quantities of a substance exert a stimulating effect does not necessarily imply that larger quantities would be beneficial. In the animal organism, for instance, a small amount of alcohol is known to produce the effect of stimulation, whereas larger amounts have a depressing effect. The same may be said of ether and chloroform. With plants, there are several well known examples of the same condition. Katayama [1] and others have shown that ferrous sulphate in small quantities produces a stimulation of certain plants; and whether or not this is brought about by bringing into solution some of the dormant bases of the soil, larger quantities of the same substance are often referred to as actually poisonous to the plants. [2] Sutherst [3] has shown that the application of small amounts of various manganese compounds, including the dioxide, has a stimulating effect on maize, but he points to the work of Salamone as indicating that larger amounts of these substances are detrimental.

The question of how these substances produce stimulation, in small quantities, and a depressing effect, when present in large quantities, is not thoroughly understood; but that such is the case, is generally accepted. Aso [4] for instance, has shown that a given amount of manganese may produce stimulation of rice, whereas the same amount of this element, when applied to wheat and barley, may, under certain conditions, result in decreased vigor and the development of a yellow color in the plant. This author has further pointed out that the depressing effect of such applications of manganese is usually more marked in cold weather than in warm; and with the return of warm weather, in some instances, these plants were able to entirely overcome the stunted growth and yellow color.

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1. Bul. College of Agric., Tokio Imperial University, Vol. VII, No. I.

2. "Agriculture" by Storer, Vol. I, p. 216.

3. "Manganese Compounds as Fertilizers for Maize," The Transvaal Agric. Journal. Vol. VI, No. 23.

4. Bul. College of Agric., Tokio Imperial University, Vol. V, No. 2, pp. 177-185.

We find a parallel condition at Wahiawa, where the pineapples on soils which contain an intermediate quantity of manganese, have been repeatedly observed to become decidedly yellow during the winter months; but such plants sometimes entirely overcome this condition with the return of warm weather. It should be mentioned in this connection that sugar-cane grows exceedingly well on these manganese soils, where the pineapples refuse to grow.

Bertrand [1] some years ago, found that the ash of oxidizing enzymes contains considerable amounts of manganese, and that the addition of soluble manganese salts to the oxidase greatly accelerated their oxygen carrying power. Woods [2] has shown that the yellow spots, which sometimes occur on leaves of certain plants, have a greater oxidizing power than the green parts of the same plant. In seeking an explanation of the yellow color produced by the application of manganese sulphate to barley, Loew and Sawa found that such plants are more vigorous oxidizing agents than those not treated with manganese. Summarizing these effects, they say: "Manganese exerts, in moderate quantity, an injurious action on plants, consisting in the bleaching out of the chlorophyl. The juices of such plants show more intense reactions for oxidase and peroxidase than the healthy control plants. Manganese exerts further a promoting effect on the development, still observable in high dilution, while the injurious effects disappear under this condition. It is probably that soils of great natural fertility contain manganese in an easily absorbable condition, and this forms one of the characteristies of such soils." [3]

With the view of ascertaining whether yellow pineapple plants are more vigorous oxidizing agents than the green plants, a small portion of both yellow and green leaves were macerated with crushed glass, allowed to stand about an hour, and the ex-

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1. Compt. rend. Vol. 124, Page 1032.

2. Abstracted in E. S. R. Vol. XII, p. 216.

3. Bulletin, College of Agriculture, Tokio Imperial University, Vol. V, No. 2, p. 172.

tract was tested for oxidase, using the guiacum and aloin tests; the following table will show the results:

TABLE VI.

	Guiacum	Aloin.
Yellow leaves	Deep blue.	Rose red.
Green leaves	Pale blue.	Faint red.

It is thus shown that the plants grown on the soil containing high percentages of manganese, contain a more active oxidase than plants from soil containing little manganese; and whether the increased activity of the oxidase in the yellow plants brings about their etiolated appearance, by the actual oxidation of the chlorophyl, or for other reasons, cannot be positively stated at this time. An examination under the high power miscroscope of the cross-section of the yellow leaves, shows, however, that for the most part the chlorophyl bodies have been entirely destroyed. Further investigation it is hoped will throw more light on this subject.

SUMMARY AND CONCLUSIONS.

1. Some of the pineapple soils of Hawaii contain black spots on which pineapples do not grow successfully.

2. The application of fertilizers and lime in conjunction with good tillage and drainage, has not resulted in effectually overcoming the yellow appearance of the pines on black soil.

3. The black soils contain less acidity than the red soils.

4. There is but one important difference in the chemical composition of these soils, viz., in regard to the manganese content. The black soils contains many times as much manganese as the red soil.

5. The black color of these areas may in part be attributed to the presence of higher oxides of manganese.

6 There is a close correlation between the degree of yellowing of the pines and the percentage of manganese in the soil.

7. Yellow pines from soils containing a high percentage of manganese are more active oxidizing agents than green plants from red soil.

8. The yellow pines have a poor root system and contain but little chlorophyl.

9. As yet no positive remedy for this condition has been worked out. It seems wise to try other crops on the black soil, especially since sugar-cane grows well on the black soil.

This investigation is being continued along the lines suggested in the body of this bulletin. Acknowledgments are due Miss Alice R. Thompson, Assistant chemist, for assistance in this work. A large part of the analytical work was done by her, and many valuable suggestions were offered from time to time. Also to Doctor E. V. Wilcox for the microscopic examination of these plants, and for many very valuable suggestions. Thanks are also due the pineapple growers at Wahiawa for cooperation in this work.

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